A

Research Proposal

on

"Interaction of Organophosphate Pesticides with Essential Metal ions and its Environmental Impacts"

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1. INTRODUCTION

Organophosphate pesticides (OPs) are the ester forms of phosphoric acid usually considered as secure for agriculture uses due to their relatively fast degradation rates.[1]Although the degradation of OPs is a linear function of microbial composition, pH, temperature, structural arrangement etc. OPs inhibit acetylcholinesterase (AChE) activity not only in insects only, but can also affect the nervous system of other organisms as well as humans.[1-3]

Literature data illustrated the OPs persistence in soils years after their application. But the reason behind this environmental persistence is not very clear, it has been observed in last decade overuse/long usage of pesticides harmed the soil quality/fertility, especially due to highly acidic pesticides like OPs. Pesticides form the complexes with soil micronutrients or *trace metal ions*, which is most unscrutined part of pesticides, it makes the OPs unavailable for microbial metabolism, as a results conserved in soils and transferred to humans through food.[4]

The almost unviewed part of OPs and other pesticides is the "chelating effect" of these pesticides with the micronutrients of soils. This turns our interest in this topic because it will be the major threat and challenge for the future, to identify and overcome the problem of the deficiency of micronutrient in crops, eventually in humans due chelating action of pesticides, which hinders the growth of crops as well as humans. In nut shell the chelating action of the pesticides causing the deficiency of micronutrient *viz.* manganese (Mn), iron (Fe), cobalt (Co), copper (Cu), molybdenum (Mo) etc. in plants consequently in humans.[5, 6]

1.1a. Significances of Pesticides

There was the time after the Second World War when whole world was in the grip of hunger and misery.[7] To overcome the problem of hunger, mission "Green Revolution" had been introduced. Due to enormous efforts and firm work of the whole world "Green Revolution" had been launched successfully. As a result, world start restructure at very fast rate on the basis of agriculture.[8 - 10] The major weapons of the "Green Revolution" were the "synthetic pesticides" *viz.* Organochlorines, Organophosphates and Carbamates.[11 – 13] At that time perhaps no one was awaked about the hazards effects of all those pesticides used. Today these are the consequences of all those pesticides that were used in the last five decades, the number of environmental and health issues have aroused the public concern. Among these,

the overuse of pesticides is major concern, especially in relation to the health and environment.[14 -19] For the experts and scientific society; it is the matter of huge concern, challenge and threat.

1.1b. Pesticides as a Necessity of Time

In the 1960s, use of the pesticides was the obligation but; it is necessity of present and future because of following facts: [20-22]

1. To nourish the fast mounting population.
2. To ascend the economic growth of agriculture based countries.
3. To increase the quantity as well as quality of agriculture based products.
4. To control the seasonal & epidemic diseases.
5. To overcome the problem of storage of eatable & food grains.

1.2. Significance of Metals Ions w.r.t. Plants and Humans

Metals are an integral and specific part of many structural and functional components in the plants and human body to complete the healthy life cycle. As we know that the crops products are the main source of trace metal ions of humans and trace metal ions of the soil are main nutrient for the plants. Think for a moment, if there is no manganese (Mn) ion (Z = 25)? There would be no photosynthesis hence "no plants, no oxygen and no life." [23] Think if there is no iron (Fe) ion (Z = 26)? There would be almost zero growth of plants and human beings and no iron content present in food nutriment hence disease due to deficiency of iron like anemia become health problems to world.[24, 25] It is not about the Manganese and Iron, but it is about the all essential or trace metal ions because each ion has its utility and functions. Ultimately deficiency of metal ions among the living beings cause the number of disease, hence life would become miserable and drastic. Number of living beings looses their health level and their lives directly and indirectly. The major source of metal ions for the humans is the agro-products; primarily the crops based agro-products.

1.3. Influence of the Pesticides on the Plants Micronutrients

As pesticides are used to protect the crops from their predator, but the residues in air and persistence of these pesticides in the soil effects the life cycle of non targeted species also.[2] As per literature the degradation of the pesticides governed by the factors likes microbial composition, pH, temperature etc.[3] In soil pH is an important factor which influence the

complex formation and stability, for example uptake of manganese decreases with increased soil pH and is adversely affected by high levels of available iron in soils. Uptake of iron decreases with increased soil pH, and is adversely affected by high levels of available phosphorus, manganese and zinc in soils. Zinc uptake by plants decreases with increased soil pH. Copper uptake decreases as soil pH increases. Increased phosphorus and iron availability in soils decreases copper uptake by plants. Uptake of zinc also is adversely affected by high levels of available phosphorus and iron in soils. Molybdenum uptake by plants increases with increased soil pH, which is opposite that of the other micronutrients.[26, 27] Organophosphates are the pesticides having moderate to low pH i.e. acidic in nature. Hereby organophosphate pesticides are affects the soil pH consequently uptake of trace metal ions affected. Therefore organophosphates pesticides having the three fold hazardous effects:

1. Acidifying the pH of soil as a result the uptake of micronutrients stalled.
2. Lowering of soil fertility by acidifying the pH of soil.
3. After their degradation by soil bacteria converted into phosphate moieties which causing the acidification of pH and production of toxic moieties cause environmental pollution.
4. Chelation with trace metal ions of soil which leads to poor growth of plants consequently poor growth of humans.

Considering the chelating effect as the foundation of our study, in current topic we are going to explore the study on the Coordination Chemistry of Trace Metal Ions with the Acephate, Glyphosate, Monocrotophos & Phorate (*Figure* **1**) and their Environmental Impacts.

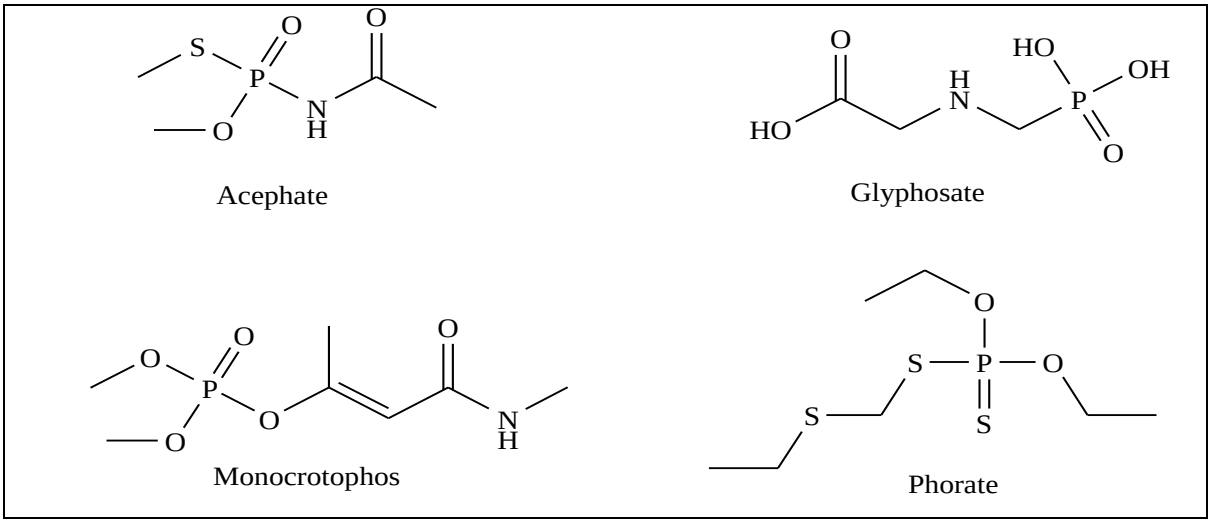


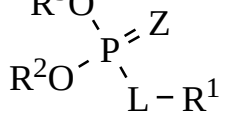
Figure **1**: Structure of Acephate, Glyphosate, Monocrotophos and Phorate.

2. LITERATURE REVIEW

Organophosphates belong to the broad family and having their own history of development, utility, benefits, hazards, toxicity, mode of action etc. In the past organophosphates literature has been reviewed over the years by practitioners of a variety of chemistry-related disciplines that included, remediation catalysis,[28] agent decontamination,[29] liquid chromatography mass spectroscopy (LC-MS),[30] AChE reactivation,[31-35] agent detection,[36] agent (bio)decontamination,[38-43] agent degradation,[44-46] complex-formation,[47] environmental chemistry,[48] bioremediation,[49-51] biosensing,[52] nano-based decomposition,[53] biomonitoring,[54] toxicity,[55-57] NMR spectroscopic analysis,[58] surface adsorption,[59] ozone-mechanism based degradation,[60] biodegradation. [61]

2.1. Basic Structure of OPs

Organophosphate pesticides derived from phosphorus analog PH_3 having phosphorus as a core nuclei involved in oxidation states III and V. Basically organophosphate (*Figure* **2**) is the general name for esters of phosphoric acid. Hydrolyzed derivatives of phosphorus formal incorporation of additional oxygen atoms gives phosphinic acid ($O=PH_2OH$) and phosphonic (phosphorus) acid [$O=PH(OH)_2$]. Notably, these species may tautomerize between P(V) and P(III), that is, $H_2P(O)OH$ to $HP(OH)_2$.



Z = O or S
R = Me/Et etc.
LR^1 = Leaving groups, *viz.*
Alkyl, Alkoxy, Alkylthio, Aryl, Hetrocyclic, Aryloxy, Arylthio etc.

Figure **2**: Basic structure of OPs.

Also a tetrahedral structure [$O=PH(OH)_2$] is more established than its isomer phosphonic acid, $P(OH)_3$. This form can be stabilized by coordination with some metals.[62] Classes of OPs are (*Figure* **3**) *viz.* phosphates, amidates, thionates, thiolates, phosphonates and phosphinates.

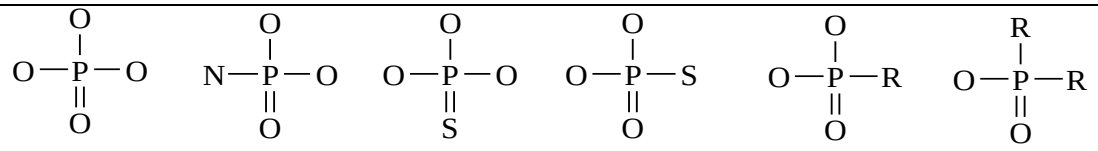


Figure **3**: Different basic species of OPs.

2.2. Toxicology

Acetylcholinesterase (AChE) inhibition is the most illustrious mode of action of the organophosphates. Inhibition occurs through the irreversible binding of organophosphates to the catalytic site of the enzyme.[63-65] Three basic types w.r.t. organ system of organophosphate pesticides toxicity are seen i.e. Parasympathetic nervous system, Nicotine-receptors system, Central nervous system. In all these three the basic mechanism of toxicity is inhibition of acetylcholinestrage due to phosphorylated action of OPs, causing AChE inactivation in an irreversible manner. Enzymatic hydrolysis (*Figure* **4**) involves nucleophilic addition and acid-based reactions at the catalytic site of the enzyme that involves a catalytic chord i.e. three amino proteins *viz*. serine, glutamic acid, and histidine.[66]

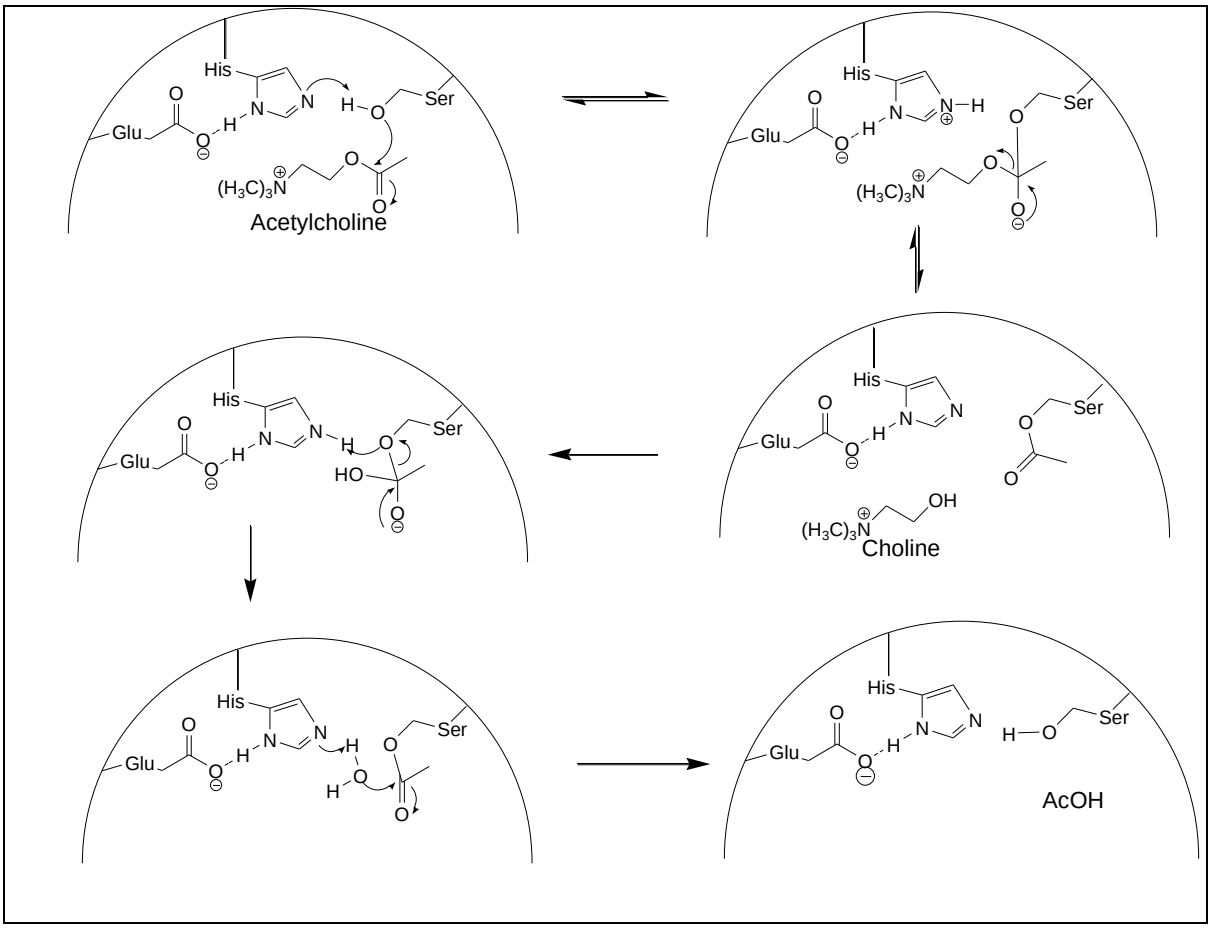


Figure **4:** Acetylcholinesterase Hydrolysis of Acetylcholine.

An enzyme-substrate complexation between acetylcholine (ACh) and the enzyme form by electrostatic attractions between the positive charge on the ACh nitrogen and the negative charge in the acidic site. Then the imidazole moiety of the histidine catalyzes acetylation of

the serine hydroxyl group; the acetylated enzyme then allows for nucleophilic attack by water to transpire. The deacetylation reaction results in the liberated enzyme and release of inactive choline and acetic acid. Catalytic activity of AChE is very high with a turnover number of $>10^4$ $s^{-1.67}$

The mechanism of AChE inhibition with organophosphates (*Figure* **5)** is analogous to the reaction of enzyme with ACh, excluding for the reaction in which the leaving group of the organophosphates is lost, so the enzyme becomes phosphorylated instead of acetylated.[68, 69]

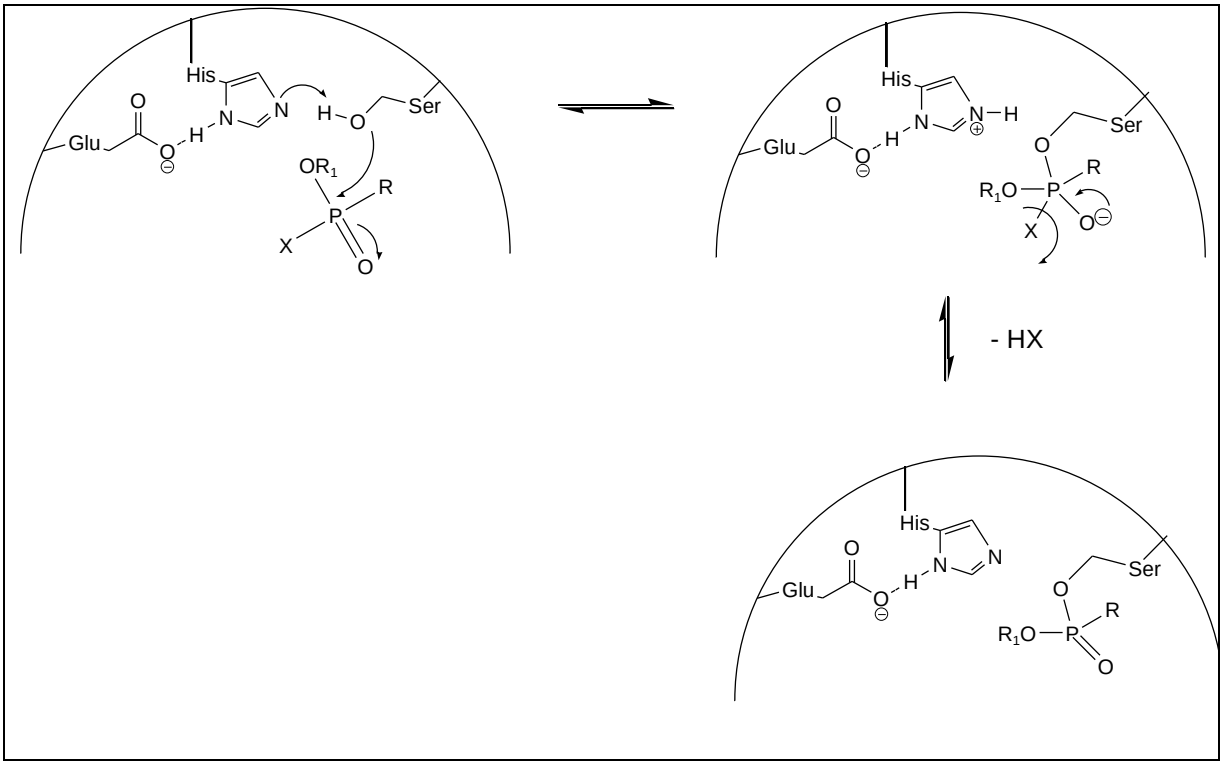


Figure **5**: Inhibition and "Aging" of AChE with OPs.

Phosphorylation is a two-step addition-elimination reaction in which the addition step is rate-determining, while the elimination process is faster. It should be noted that phosphorylation occurs via a *trigonal bipyramidal* intermediate, whereas in the case of acetylation is anticipated through a *tetrahedral* intermediate.[70-72] The irreversibly inhibited phosphorylated enzyme can no longer hydrolyze acetylcholine. This leads to an accumulation of acetylcholine in cholinergic receptors and consequent continuous stimulation of the nerve fiber. Phosphorylated AChE having the stable bonding and forces than acetylated one, but it can undergo a possible secondary process. Among these first one is the reactivation-hydrolysis of phosphorylated enzyme. But the rate of hydrolysis is much slower than in the

case of an acetylated enzyme.[73]Another mechanism is the breaking of the PO-C bond the inhibited enzyme known as "aging".[74, 75]

2.3. Decomposition

2.3a. Hydrolysis

Alkaline hydrolysis rates are much faster than the corresponding rates under neutral conditions because reaction is initiated by the nucleophilic attack of the hydroxide ion at the phosphorus atom. The reaction depends on the electron deficiency of the phosphorus atom, which may be affected by the electronic properties of substituents on phosphorus. Thus, the hydrolyzability of the esters is increased by the presence of electron-withdrawing groups and is decreased by the presence of electron-releasing groups.[76]

The majority of organophosphorus pesticides are phosphorothionate esters, which are generally 2 to 20 times more stable than the corresponding phosphate esters. Sulfur is around 1.4 times less electronegative than oxygen, and therefore the phosphorus atom of phosphorothionate esters is less electrophilic and consequently less reactive with water or hydroxide ion.[76, 77] The rate of hydrolysis for organophosphorus esters is independent of pH in the acidic range (1-5) and they tend to be very stable under such conditions. Conversely, they are much more unstable under alkaline conditions. The hydrolysis rate increases steeply at pH higher than 8 to 12. Since the hydrolysis is primarily catalyzed by hydroxide ion under alkaline conditions, the hydrolysis rate increases around tenfold with each additional pH unit. Rates of hydrolysis are also affected by temperature.[78] In the trialkyl Phosphates case, both alkaline and acidic conditions hydrolyze via nucleophilic attack on the phosphorus, whereas in neutral solutions preferential attack on the α-carbon occurs instead of P. Only in the case where competing nucleophiles of a "hard base" type does attack occur on the phosphorus "hard acid".[79] Additional mechanisms of note include the amidates, where under basic conditions the nitrogen is free to participate in π-bonding with phosphorus, thus making the center more stable. However, in acidic solutions the nitrogen is protonated and hydrolysis via amino-P cleavage readily occurs. A phosphorus-carbon bond of phosphonates enhances hydrolysis at high pH because the alkyl group is non-polar and carbon does not participate in π-bonding with phosphorus, placing greater polarity between the P-O bonds. On the other

hand, phosphonates and phosphinates are comparatively more stable in acidic conditions than the phosphates.[80]

Almost all Organophosphates react with water at different pH which can be considered as a basic method for detoxification and decomposition of OPs.[81-83] Hydrolysis proceeds by phosphorus SN^2 nucleophilic attack (*Figure* **6**). The hydrolysis of Fenthion, phoxim, Dichlorvos, azinphos-methyl, diazinon and parathion-methyl has been studied at different pH and temperatures. It was observed that hydrolysis is a dependent function of pH, temperature, chemical structure and functional groups of a pesticide molecule.[84-89] This reaction most probably gives the non-toxic byproducts.

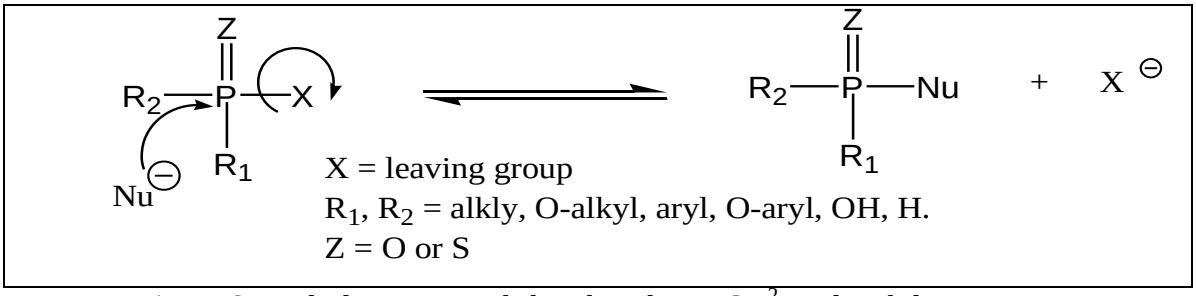


Figure **6**: Hydrolysis proceeds by phosphorus SN^2 nucleophilic Reaction.

Computational studies on the solvolysis of nerve agents also indicate that the P-O and P-SR bond cleavage processes are kinetically competitive, but the P-SR cleavage pathway is sympathetic over P-OEt bond cleavage by the energy difference of 3.2 Kcal/mol.[90, 91]

2.3b. Peroxide

Basic unit of peroxide is R-O-O-R. Peroxides are basically non toxic, non corrosive and having low freezing point, hence these are considered as attractive moiety for decomposition and detoxification of OPs. Decomposition reaction (*Figure* **7**) follows the nucleophilic pathway.[92, 60]

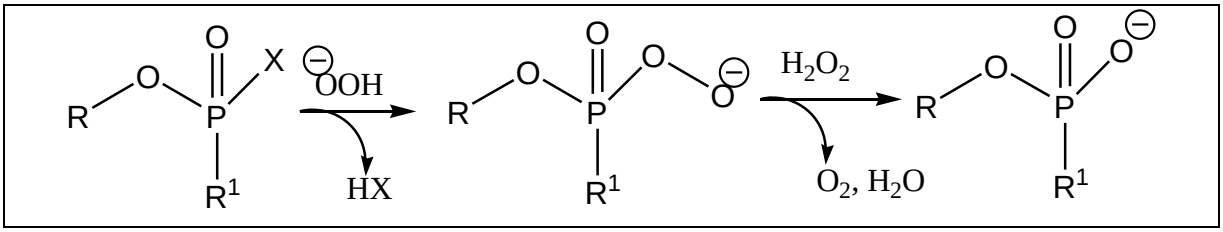


Figure **7**: Nucleophilic Pathway of Peroxides.

This method considered as more attractive than simple hydrolysis towards OPs.[93-95]As per literature the rate of detoxification of the malathion, diazinon, parathion and mevinphos is directly proportional to the concentration and pH (>10).[96-98]

2.3c. Metal-Catalyzed Reactions

The mineral-surface-catalyzed hydrolysis and divalent metal ion-catalyzed hydrolysis of thionate (P=S) and oxonate (P=O) organophosphorus pesticides at different pH has been examined in light of three possible catalysis mechanisms : (1) metal ion coordination of the thionate sulfur or oxonate oxygen to enhance the electrophilicity of the phosphorus electrophilic site; (2) metal ion coordination and induced deprotonation of water to create a reactive nucleophile ; and (3) metal ion coordination of the leaving group to facilitate its exit. Results indicate that pH alone cannot be used as a single parameter to predict the hydrolysis of OPs, other parameter such as temperature, metal content and water quality also showed significant effect on the hydrolysis rate.[99-106]

In case of Metal Catalyzed action P-O bond cleavage by metal/ metal complexes,[107] The metal-catalyzed hydrolysis literature is widespread, stemming from the ubiquity of phosphates in biology, that is, in the backbone of DNA/RNA, which may be cleaved hydrolytically throughout the use of metal complexes. Metal like Cu^{2+}, Co^{2+}, Zn^{2+}, Mg^{2+}, La^{3+}, Sm^{3+}, Eu^{3+}, Yb^{3+}, Mo^{2+}, Zr^{4+}, Ce^{4+}, Hf^{4+} and Th^{4+}studied for the decomposition of pesticides at pH 8-10 and temperature 25-70^{0}C.[108-119] Metal like Al^{3+}, Cr^{3+}, Co^{2+} and Mn^{2+} reported in the presence of O_3 involved in PO-R bond cleavage.[120-123]

2.4. Methods of Detection of OPs

The combination of FTIR, NMR and Mass data is often sufficient to determine completely the structure of an unknown molecule. There has been a longstanding interest, first among inorganic chemists, about how organophosphates bind to metals, and next by analytical chemists, about how an adequate detection device can be engineered. Ligand optimization and reporting media continue to be explored in OPs detection efforts that involve various spectroscopic techniques such as UV-Visible, FTIR, Mass and NMR spectroscopy.

2.4a. UV- Visible Spectroscopy

In the field of pesticides UV-Vis. Spectroscopy play the vital role in the detection and interaction of metal ions with organic ligands i.e. pesticides, especially with transition metal

ions. P=O can obscure absorbance. Agents themselves are not significant absorbers or emitters in the UV-Vis spectral region[124] unless they are specifically modified with, e.g., a fluorescent coumarin-type leaving group.[125,] With the inclusion of a photoabsorber material, such as a porphyrin, Photocatalytic degradation of acephate and monocrotophos in the presence of TiO_2 indicated that indicates that the decomposition of acephate begin from the destruction of C-N and P-N bonds.[126-130] The $ZnFe_2O_4$-TiO_2 composite photocatalyst is prepared by sol-gel method and used to degrade acephate successfully.[131] Cu(II)-Glyphosate complex was studied in tea at pH 5 at absorbance 250 nm.[132] A UV-Visible based study to detection of monocrotophos at 490 nm included the effect of temperature and different regent *viz*. 2, 4, dinitrophenylhydrazine and NaOH at different pH level.[133] The photolysis of phorate has been studied as a thin film on a glass surface and in a solution of methanol-water (60:40) by ultraviolet light ($\lambda > 290$ nm). The rate of disappearance of phorate in the solution show first order kinetics with a rate constant of 4.9×10^{-5} s^{-1}.[134] Metal complexes of Fe(III), Al(III), Co(II) and Zn(II) studied by using UV-Spectrophotometer, it observed that the complexes of methylphosphonic acid, formed the M-$(CH_3PO_3)_3 \cdot 3H_2O$, and aminomethylphosphonic acid, formed the M-$OH(NH_3CH_2PO_3)_2 \cdot H_2O$. Also complexes of *N*-phosphonomethylglycine were prepared and the formula was M-$OH(-OOC-CH_2-NH_2^+-CH_2-PO_3^{2-}) \cdot 2.25H_2O$ is proposed. UV-Vis. study indicating that the complexes form by the chelation of P=O and N-H bonds by consuming two ligands and two water molecules.[135]

2.4b. FTIR Spectroscopy

IR spectroscopy is indispensible for many systems mentioned herein; direct access to monitoring the phosphoryl stretch is very useful. Electron-poor ions such as Fe(III) and Cu(II) favor stronger coordination and give [P=O] stretching frequencies concomitantly lower by 30-100 cm^{-1}. Some other functionality, such as perchlorate Cl-O stretches, can obscure P=O absorbance. In OPs from literature following main stretching and bending frequencies observed in different solvents.[136-138] OPs having the thio as well as amino salts, for the thio group ν(S-H) and ν(C-S) observed at 2550 and 730 cm^{-1}. Ammonium salts are divided into following parts as per their IR frequencies; these are primary, secondary and tertiary ammonium salts. In all these salts ν(C-N) observed between the region 1380 – 1250 cm^{-1} and ν(N-H) between the 1550 – 1630 cm^{-1}. For the ammonium salt a strong band of

ν(N-H) at 1430cm^{-1} also reported in literature.[139] In the FTIR study of copper complexes, for the yellow complex; [Cu(Ph_3P=O)$_2Cl_2$] the ν(P=O) observed at 1142 cm^{-1}. For the dark red complex;[Cu(Ph_3P=O)$_2Br_2$] the ν(P=O) observed at 1145, 1169 cm^{-1}. For free Ph_3P=O, ν(P=O) is 1195 cm^{-1}. These compounds were found to be *tetrahedral*. The cation moiety Cu(II)-(Me_3PO)$_4$ was *square planar*. Arsenic analogs were yellow-brown (ν(P=O) at 840 cm^{-1} and olive green (ν(P=O) at 842 cm^{-1}). Perchlorate species were also obtained, but the C=O stretching bands in the IR spectrum obscured the P=O stretches. In MgI_2 complex with diphenylphosphinates; it was found that the PO-C bond, not the P-OC bond, was cleaved.[140-146] In the interaction of Cu(II) with DIMP the IR frequency of ν(P-O) and ν(P-O…H) observed at 1016 and 1206 cm^{-1}.[147] Metal complexes of Fe(III), Al(III), Co(II) and Zn(II) studied by using FTIR, it observed that the complexes of methylphosphonic acid, formed the M-(CH_3PO_3)$_3$·3H_2O, and aminomethylphosphonic acid, formed the M-OH($NH_3CH_2PO_3$)$_2$·H_2O. Also complexes of *N*-phosphonomethylglycine, were prepared and the formula was M-OH(−OOC–CH_2–NH_2^+–CH_2–PO_3^{2-})·2.25H_2O is proposed. FTIR study indicating that the complexes form by the chelation of P=O and N-H bonds.[135] In the FTIR study of interaction of OPs herbicide glyphosate with Fe(III) in aqueous solution at pH 4, suggests that coordination of Fe(III), or more likely Fe(OH)$^{2+}$ species, occurs through the phosphonic group, glyphosate shows no evidence of coordinating the metal through the carboxylate anion or the amino group; however, significant changes are observed in the range for the phosphonic group vibrations as expected for metal-phosphonate coordination.[148]

2.4c. NMR Spectroscopy

N**uclear magnetic resonance (NMR)** is a spectroscopic method that is even more important to the structure elucidation than other spectroscopic techniques. Many nuclei may be studied by NMR techniques *viz*. ^{13}C, ^{1}H, ^{31}P, ^{15}N, and ^{19}F. Any atomic nucleus that possesses either *odd* mass, *odd* atomic number split in the radiofrequency region. NMR gives information about the number of magnetically distinct atoms of the type being studied.[135] NMR spectroscopy supports many areas of chemistry and science. NMR spectra have found great utility in monitoring reactions and characterizing new compounds and also in detection of OPs and their fragments.[149, 150] There are numerous nuclei that can be brought to bear in OPs studies, especially the ^{31}P nucleus. Analytes that contain characteristic ^{13}C, ^{1}H, and ^{31}P, as

well as ^{15}N and ^{19}F, NMR signals can be probed.[151] Other NMR active nuclei and related experiments also are found in the literature. The types of experiments have involved HSQC NMR,[152-154] as well as magic angle spinning.[155] Next, shift reagents can change the phosphorus δ value.[156] One early study involved mixtures of $(Me_2N)_3P=O$, DMMP, or $(MeO)_3P=O$, in the presence of Be^{2+} and Al^{3+} ionic centers and a series of phosphates was treated with Co^{2+} and Fe^{3+}.[157, 158] The species$(MeO)_3P=O$, $(EtO)_3P=O$, and $(MeO)_2P=O(Me)$ were all found to give shifts upon binding; also P-H decoupling was observed. With this technique, changes in P-S bonding can be monitored.[159] Variable-temperature ^{31}P NMR spectroscopy was used in studying resin-based systems with two DMMP adsorption sites, the macro-reticular region and the quaternary ammonium hydroxide ion-exchange sites.[160, 161] It was found that DMMP may migrate from one site to another. There is also a report of lanthanide-induced shifts from authors who have also been active in the organophosphonate sensor area.[162] An NMR spectroscopic assay was also developed to conveniently determine the purity of live agents of OPs derivatives. ^{31}P NMR spectroscopy can also be used in studies that involve enzymes that degrade agents.[160, 163] Studies that successfully determine discrete cleavage events have used ^{31}P.[163] Nuclei other than ^{13}C, ^{1}H, and ^{31}P NMR also occasionally hold prominence. The ^{27}Al, ^{113}Cd, and ^{199}Hg nuclei have been utilized in terms of monitoring the adducts and mineralization.[164,165] A ^{1}H-NMR study of phorate deals to photodegredation of phorate, indicated the P-S bond destruction.

2.4d. X-ray Diffraction

X-ray diffraction is among the unswerving techniques to studies and elucidates the intricacies of metal ligand structure and probable binding possibilities that help open up a casement for future sensing possibilities. In study of $[R_3P=O---M^{n+}]$ moieties (R = alkyl, aryl) and (M = any metal), the mean P=O bond length in $[P=O---Mn^{+}]$ interactions is 1.48 Å and the mean M---O bond length is 2.33 Å.[166-168] The importance of these structures is that they resemble a deprotonated acid fragment bound through three atoms to one metal center. $(CH_2)_2$ could be thought of as holding the place of [-P=OMe(OR)-]. This motif is pragmatic with respect to a degraded sample in which the (-OR) has been hydrolyzed off. Metal complexes of Fe(III), Al(III), Co(II) and Zn(II) studied by using XRD-Spectrophotometer, it observed that the complexes of methylphosphonic acid formed the $M-(CH_3PO_3)_3 \cdot 3H_2O$, and

aminomethylphosphonic acid, formed the M-OH$(NH_3CH_2PO_3)_2 \cdot H_2O$. Also complexes of *N*-phosphonomethylglycine were prepared and the formula was M-OH$(-OOC-CH_2-NH_2^+-CH_2-PO_3^{2-}) \cdot 2.25H_2O$ is proposed. X - ray study representing that metal ions concerned in octahedral structure.[135]

2.4e. Electrochemical

Almost all current instrumental techniques that explicitly determine the presence of pesticides are generally exclusive and non-portable, such as FTIR, mass chromatography and NMR spectrophotometer etc. But electrochemical methods are simple, versatile, in terms of controlling and altering the behavior of redox materials. Transition metal ions here have vulnerable properties. Such equipment is not too bulky and has a portable device, principally in regards to recent lab-on-a-chip research efforts. Reviews in this area mostly deal with biosensing. Organophosphonate electrochemistry with sarin, $(EtO)_2(EtSCH_2\text{-}CH_2S)P=O$, parathion, and malathion. There were reports of a mercury surface with which polaragram data was recorded. Chemical groups point outward and waters are replaced stepwise in a Cu^{2+}-complex by the surface-active compounds $R_3P=O$. In the late 1990s, there are outstanding electrochemistry papers concerning with organophosphorus hydrolase.[169-172] Also, some studies involve the use of phthalocyanines. Thus, this section involves structurally positioned redox active metal ions that do not directly bind with OPs donor atoms. Recently, electronic tongue array, consisting of an eight working electrodes (Au, Pt, Ir, Rh, Cu, Co, Ni, and Ag) was used to detect nerve agent stimulants DCP and DECP in aqueous environments.[173]

2.4f. Mass Spectrometric

The fundamental principles of mass spectroscopy (MS) to determined the mass-to-charge ratio of the molecule by ionizing it by using different procedures. The number of ions with a particular mass-to-charge ratio is plotted as a function of that ratio. The types of MS techniques include MALDI-TOF, GC-MS, ESI, SPAMS, and desorption electrospray. MALDI-TOF and MS-TOF was presented as an effective way of determining widespread emergency events.[139] A detection by MS of species that include $(RO)_2P=O(R_1)$, $(RO)P=O(R_1)F$, $(RO)P=O(R_1)(SR_2)$, and $(R_2N)P=O(OR_1)(CN)$.[175] MS also provides support for some surface-based studies. The detection of DMMP on Pt was supported by MS

techniques; it was shown that DMMP was bound to the surface in that it was able to desorb and be detected intact. Also, a Mo surface was monitored for DMMP desorption products using MS.

A study include the development and inter-laboratory verification of LC–MS libraries for organic chemicals of environmental concern, includes the 129 pesticides in which the monocrotophos and phorate having the m/z at 193, 98 and 75. In the study it was observed that more than 90% data was accepted in both modes.[170] The determination of OPs in human blood and water using solid-phase microextraction and gas chromatography with mass (GC-MS) spectrometric detection performed.[176-179] A Multiresidue detection of pesticide in fishery products was conducted by using the tandem solid-phase extraction technique. Study includes more than 50 OPs. Zero recovery was obtained from samples fortified with acephate and monocrotophos and 118.2 and 125.4 % in sample amino-propyl, the maximum label spiked (mg/L) for both is 5.[180] Method validation and comparison of acetonitrile and acetone extraction for the analysis of 169 pesticides in soya grain by liquid chromatography–tandem mass spectrometry.[181]

The interesting disulfide derivative [bis(diisopropylaminoethyl)disulfide] was determined from a soil sample (detected at 1 μg per 1.0 g of soil).[182] Secondary ionization (IM-TOF-MS) was used in detecting DMMP, pinacolyl methylphosphonate, diethyl phosphoramidate, and 2-(butylamino)ethanethiol.[183] Some reports involve the mention of pesticides: malathion was studied with GC-FID.[184] ES-MS was used to support microsynthesis of various O,Odialkyl-N,N-dialkylphosphoramidates to generate a library of mass spectra.[185] Additionally the methyl esters of N,N-dialkylaminoethane- 2-sulfonic acids, $R_2NCH_2CH_2S(O)_2OCH_3$, were analyzed by GC-EI mass spectroscopy.[186] Rapid determination of pesticide residues in Chinese materia medica using QuEChERS sample preparation followed by gas chromatography–mass spectrometry.[187] In a minipig model, plasma was used in studying (iPrO(P=O)Me-(OH)) and cyclohexyl-O(P=O)Me(OH). In another study, albumin was studied; peptide fragments of human serum albumin were analyzed in response to chlorpyrifos oxon, dichlorvos, diisopropylfluorophosphate, and sarin.[188-190] Complexes of Ni, Co, and Fe, were evaluated for the OPs sensing, but Cu^{2+} gave the best response indicating

that the ligand had to accommodate enough vacancy. Thus, at this early point it was concluded that "copper complexes may adsorb and desorb phosphorus esters in air."[191-193]

2.5. Classification of Nutrients essential for plant growth

There are sixteen essential nutrient elements crucial to grow of plants/crops. Three essential nutrients are carbon (C), hydrogen (H) and oxygen (O_2) taken up from atmospheric carbon dioxide and water. The other 13 nutrients are taken up from the soil, often grouped as primary nutrients, secondary nutrients and micronutrients.[194, 195]

2.5a. Primary nutrients are nitrogen (N), phosphorus (P) and potassium (K) these are frequently found in fertilizers. Primary nutrients are utilized in the largest amounts by crops, and therefore, are useful at superior rates than secondary nutrients and micronutrients.

2.5b. Secondary nutrients are calcium (Ca), magnesium (Mg) and sulfur (S) these are required in trivial amounts than the primary nutrients.

2.5c. Micronutrients are iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B) and molybdenum (Mo) these are required in even smaller amounts than secondary nutrients.

2.6. Metal Uptake Mechanism of Plants in the Soil

The soil particles are basically of negative charges i.e. anions, so metal ions with positive charges i.e. cations, stick all over the surface of the soil particle: The root hair cells of plant roots secrete H^+ by using the water around nearby soil particles. This smaller H^+ replaces the larger macro- and micro-nutrient cations as per diffusion mechanism. The released cations are now available for uptake into roots (*Figure* **8**).

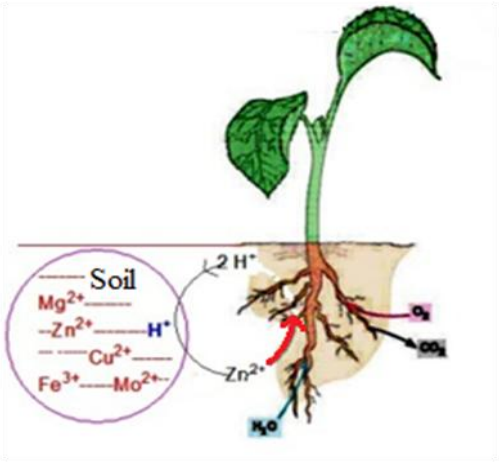


Figure **8**: Metal Uptake Mechanism of Plants in the Soil.

But this is true only for the water soluble metal chelates or metal complexes. When pesticides are mixed with the soil they adsorbed on the soil surface and form the stable complexes hence the effectiveness of soil and pesticides itself reduces. These metal complexes are decomposed if competitive chelation taken place by the other ligand having greater stability and complex formation ability.[196-206]

Among the deficiencies of micronutrients the most severe deficiencies are in zinc and iron with 50% of world cereal soils deficient in zinc and 30% of cultivated soils globally deficient in iron.[207] Solubility of particular metal complex or metal salt is governed by the pH factor of soil. As per literature for the healthy growth of the plants taken place at pH range 4 to 8.[208-210] At this pH range pesticides also form the stable complexes which are more stable than the complexes of humic acids.

2.7. Humic Substances of Soil & their Roles

Humic substances (HS) symbolize a significant proportion of organic fraction in soils. One of the most significant characteristics of HS is their ability to interact with metal ions to form water-soluble and colloidal complexes. The capacity of HS to interact with metals is recognized to their high contents of oxygen containing functional groups, such as carboxyl (COOH), hydroxyl (OH), and carbonyl (C=O). Almost every feature of the chemistry of heavy metals in soils, waters, and sediments is related in some way to the formation of complexes with HS. Thus, the availability of many metal ions, especially trace elements, to higher plants and to soil microorganisms, as well as their mobility and transport in the environment, are strongly influenced by complexation with HS.[211-214] Charge characteristics of humic substances depend upon the degree of dissociation of the functional groups. At pH < 3 HS act as uncharged polymers, whereas at pH > 3 they act as negatively charged polyelectrolytes, due to dissociation of carboxyl groups (3 < pH < 9) and phenolic hydroxyl groups (pH> 9). Chelation enhances the termination of metals from soil minerals.[215]

2.8. Chemistry of Humic Substances in the presence of Pesticides

Though, HS increases crop yield, permeability of plant membranes, uptake of nutrients, enhances growth of soil microorganisms, activates biochemical processes in plants, stimulates root development, enhances phosphate utilization of plants, has a high base exchange capacity and stimulants plant growth. These factors heave downward when

external chemicals enters into the soil environment especially pesticides. Interaction of diclofop with soil metal ions *viz*. Fe(III), Al(III) and Cu(II) was studied at pH 6.2, indicating that there was complexation taken place with metal ions and coordination sphere filled by the hydrogen bonding with water. Free pesticides also extracted from the soil, these complexes effects the soil and plant activities.[26, 27] A sorption studies of pesticides with humic acid was done using the ultraviolet derivatographic spectroscopy. The most intense interactions occurred in samples from the neutral plot, whereas the greatest effect of the humic matter in enhancing pesticide sorption was found with the calcic soil.[216] In soil the intercalation of herbicide (4, 6-dinitro-o-cresol) suggest that humic acids are constrained to the peripheral surfaces of clay. These results point toward that the humic acids play an important role in the retention of certain pesticides.[217] The interaction of aldicarb, methomyl, and ametryne with humic & fulvic acids and metal complexes of Co^{2+}, Zn^{2+}, and Sr^{2+} was studied potentiometrically and radiometrically. The order Aldicarb $\leq$ Methomyl $<$ Ametryne and complexes form were stable than complexes of humic compounds.[218] Adsorption of imazethapyr was measured onto montmorillonite clay and complexes of montmorillonite with Cu and humic acid. Adsorption of imazethapyr was found to be greater for the Cu-montmorillonite and Cu-humic acid-montmorillonite complexes than by montmorillonite alone.[219]

3. SCOPE OF STUDY

With the mount of the growth rate of population the use of pesticides has become inevitable. We acknowledge the pesticide for the same but on other side our lure for more productivity leads us towards the misuse of the pesticides which get recognized after the adverse effects on the living being. Still we have ignored the fact that these pesticides contains the active site which generally have the ability to get interact with the transition metals of the soil and leads to the formation of the complexes and may results into the either decrease or totally damage the fertility of soil. We are involving ourselves into the purposeful work of investigating the reactivity of the OPs and to overcome with the problem of interaction of OPs with the trace metals for the better scope of the fertility of the soil.

4. AIM & OBJECTIVES

1. To study the coordination chemistry of OPs with essential metal ions *viz*. Mn, Fe, Co, Ni, Cu, Zn & Mo and characterization by UV-Visible, FTIR, NMR and Mass spectroscopy.
2. To study the coordination chemistry of OPs with essential metal ions *viz*. Mn, Fe, Co, Ni, Cu, Zn & Mo in the presence of humic acid and characterization by UV-Visible, FTIR and TGA.
3. To study the coordination chemistry of OPs with essential metal ions *viz*. Mn, Fe, Co, Ni, Cu, Zn & Mo under the "cocktailed effect" and characterization by UV-Visible, FTIR, NMR and Mass spectroscopy.
4. To study the effect of OPs on plants growth in vitro/vivo.

5. METHODOLOGY

Owing to the fertility of soil, India ranks second worldwide in farm product and agriculture sector become the backbone of Indian economy. Almost every Indian state contributes towards the increased crop productivity with aid of pesticides and generally when it's come about the harmful effects of the pesticides our talks remain précised to the hazards effects on the human and other living organism. We just overlooked the fact that these pesticides which we are using have the active sites and may also effects our fertile soil by virtue of which our earth is considered as the living planet. As stated above OPs may acts as ligands. The study of interaction of OPs with the metal ions will be carried out through UV-visible spectrophotometer by evaluating the desirable shifts in the peak positions in different pH range. The metal complexes will also be synthesized in laboratory and will be characterized using FTIR, UV-Vis, NMR, EPR, Mass spectroscopy, TGA, AAS, SEM, and Single Crystal X- ray diffraction analysis. The rate determination of metal – pesticide complexation will be check by the UV-Visible spectroscopy. Before performing the reaction in lab and utilization above mention techniques, it would beneficial if selected ligands show the interaction on the Al/Si column based demonstration.

5.1. Chelating Model Demonstration of OPs

Interaction of organophosphate pesticides with the soil metal ions may result in the formation of complexes by the chelation. The chelation may easily conform by the interaction of metal ions with soil constituents (alumina & silica) in a column at suitable pH condition (*Figure* **9**).

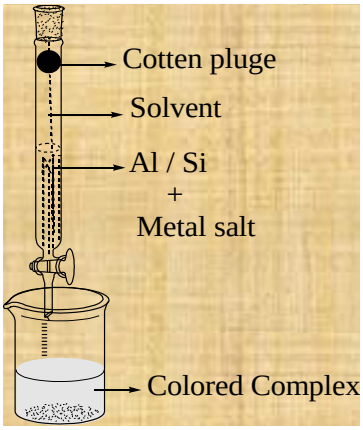


Figure **9:** Demonstration of M-OPs interaction with Si/Al column.

5.2. Mechanistic Pathway

As per literature persistence of pesticides through chelation/ precipitation/complexation; it is vary from pesticide to pesticide. In most cases the catalytic enhancement is attributed to metal co-ordination with the substrate. Several different mechanisms of catalysis by metal ions are outlined below: [99-106]

1. The metal ion acts as an electrophile and co-ordinates the Z atom (either O or S). This has the effect of enhancing the electrophilicity of the phosphorus electrophilic centre making it more prone to attack by OH or H_2O (*Figure* **10**).

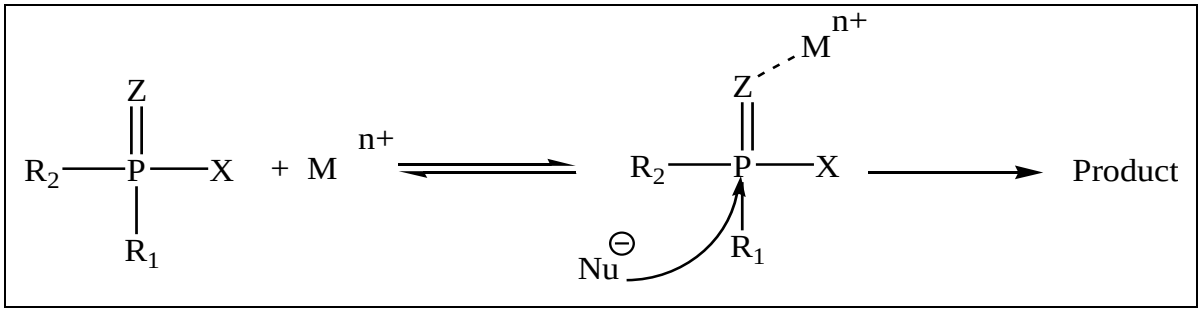


Figure **10**: Metal binding to Z, with resultant increase in the electrophilicity of phosphorus.

2. Metal ion co-ordinates the leaving group, with consequent facilitation of its departure by weakening the O-P bond (*Figure* **11**).

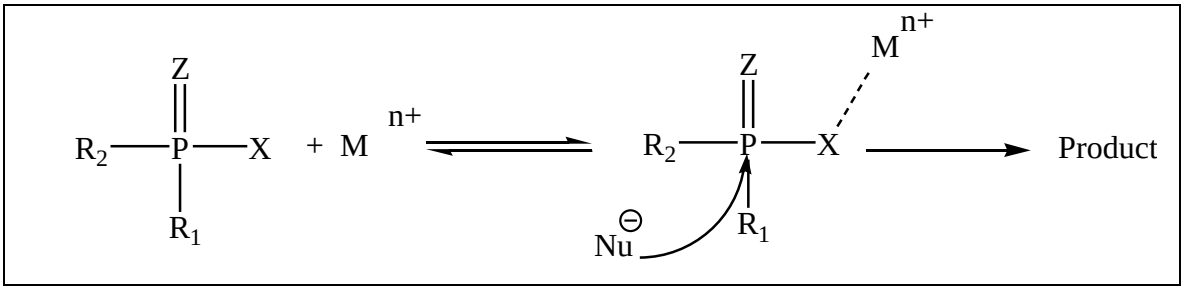


Figure **11**: Metal binding to X, with resultant facilitation of leaving group.

3. A fourth possible mechanism involves metal co-ordination of the nucleophile itself. Such a metal-hydroxide species can subsequently bind the pesticide, with resultant intramolecular –OH attack on the pesticide. This mechanism (*Figure* **13**) is more likely to be prevalent in neutral or acidic conditions where the –OH ion concentration is reduced.

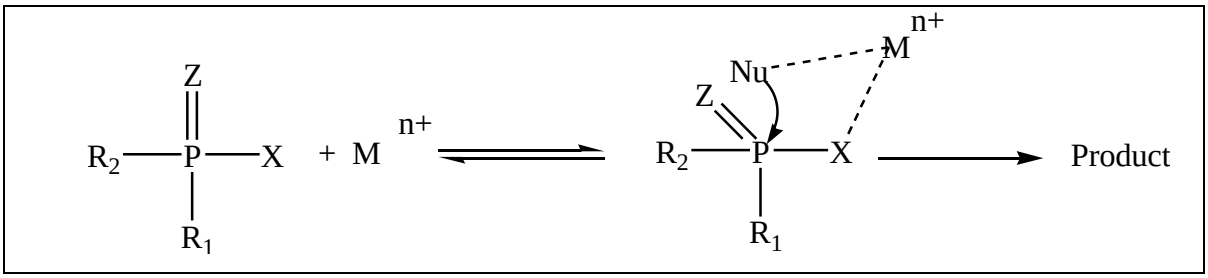


Figure **13**: Intramolecular nucleophilic attack.

4. If two ligands are present in the OP pesticide the second ligand may act as an auxiliary ligand and enable either (a) the interplay of mechanism 1 and 2, or (b) facilitate the formation of a chelates (*Figure* **12**).

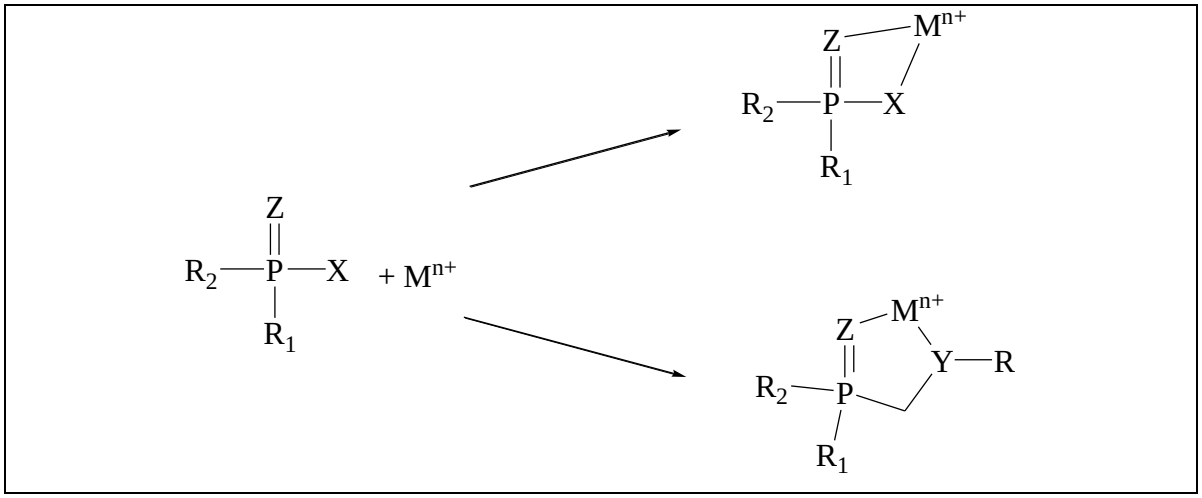


Figure **12**: Metal chelation with OPs.

A number of studies attributed the metal interactions with OPs. In most cases the catalytic enhancement was attributed to bonding between the metal cation and specific Lewis sites on the organophosphorus pesticides. These metals are known to have strong affinity for nitrogen and sulfur Lewis sites. To assist perceptive of how the metal cations co-ordination with pesticides, ESI-MS and NMR techniques were used to aid in pin-pointing metal co-ordination to the substrate. NMR enables mapping of the different electronic effects metal co-ordination has on phosphorus and proton nuclei.

5.3. Characterization of product

The combination of UV, FTIR, NMR and Mass data is often sufficient to determine completely the structure of an unknown molecule. Characterization of above synthesized product will be carried out, using combination of these physicochemical methods. In stepwise pathway, firstly UV will introduce to detect the molar ratio of interaction i.e. to

study the kinetic of metal-ligand interaction then FTIR spectroscopy will use for the detection of metal ligand bonding. Kind of bonding or environment of chelation will check by the NMR spectroscopy. Lastly the strength of bonding will be checked by using mass spectroscopy and TGA.

5.3a. UV spectroscopy

Interactions of pesticides will be followed by observing the appearance of product peaks with ultraviolet absorption both in the absence and presence of various metal ions. Interactions of pesticides followed spectrophotometrically by observing the disappearance of substrate with time.

5.3b. Nuclear Magnetic Resonance

Solution NMR is one of the principal techniques in organic chemistry used to acquire structural information about a molecule and its interactions with other elements in solution. The principle is that nuclei in the NMR resonate at a slightly different frequency depending on the electron density around the nuclei, i.e. based on the other surrounding elements. The different nuclei have the effect of either shielding or de-shielding a particular nucleus to an external magnetic field. As a result information about the chemical atmosphere of nuclei such as phosphorus and proton can be derived from its resonant frequency. NMR can therefore be used to help illuminate where co-ordination between the metal and pesticides is occurring by observing changes in the chemical shift of both proton and phosphorus nuclei. This can be achieved by conducting ^{1}H and ^{31}P experiments with and without the presence of metal ions. The principal that a change in chemical environment of a nucleus will result in a change in its resonance frequency can then be utilized to infer where interactions between the metal ions and substrate are occurring. ^{31}P chemical shifts of organophosphorus pesticides have been well characterized under the broad ppm range for the insecticides depending on structure; phosphates fall between 4 to -2 ppm, phosphorothiolates between 29-31 ppm, phosphorothionates between 60-67 ppm and phosphorodithioates between 89-100 ppm. 1H NMR studies of organophosphorus pesticides are also prevalent in the literature detailing trends in proton chemical shifts in relation to structure properties, effect of solvent on chemical shift values and coupling constants. The splitting of the phosphorus signal by coupling with neighboring hydrogens is also widely researched.

5.3c. Mass Spectrometry

Electrospray mass spectrometry in the presence of metal cations is an extremely effective technique in pin-pointing the interactions between substrate and metal. In mass spectrometry, analyte molecules are first ionized then separated based on mass/charge ratio and detected. The ionization process is extremely imperative in MS with several different types of ionization processes available including chemical ionization (CI), electron impact (EI) and electrospray ionization (ESI). Electron impact ionization (EI) is the most common ionization source used in MS work. In EI, electrically neutral molecules are transformed to molecular ions (M^{n+}) by means of high energy electrons. In EI, ionization is almost immediately followed by fragmentation of the M^{n+} ion, resulting in an intricate fragmentation model emanating from the parent ion.

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